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EUROPEAN PATENT APPLICATION

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- Minproved bleaching or detergent bleach composition.
- (5) Improved bleaching or detergent bleach compositions are disclosed which comprise a percompound, such as sodium perborate, and
 - i) a mixture of at least two peroxyacid bleach precursors

(a)
$$\begin{bmatrix} R_1(0)_n C - \end{bmatrix}_m = L$$
 and (b) $\begin{bmatrix} R_2(0)_n C - \end{bmatrix}_m = L$

wherein R_1 is a lower alkyl group containing 1-4 carbon atoms, or a phenyl group; R_2 is a higher alkyl, aryl or alicyclic radical (substituted or unsubstituted) containing 6-20 carbon atoms; n is 0-1; m is 1-4 and L is a leaving group which exerts an electron-attracting effect, or

ii) a peroxyacid bleach precursor of the formula

$$\begin{bmatrix} R_1(0)_n C - \end{bmatrix} - L - \begin{bmatrix} C - (0)_n R_2 \end{bmatrix}_{m'}$$

wherein R₁, R₂, L and n are as defined above, and m' is 1-3. The compositions show improved bleaching and cleaning effect on multistained fabrics.

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IMPROVED BLEACHING OR DETERGENT BLEACH COMPOSITION

This invention relates to improved bleaching or detergent bleach compositions which are particularly effective for washing and cleaning of fabrics at low to medium temperatures.

Detergent bleach compositions for washing at higher temperatures are well known in the art. They contain as bleaching agent normally a percompound which liberates hydrogen peroxide in aqueous solution, such as the peroxyhydrates, sodium perborate, sodium percarbonate, sodium perpyrophosphate, sodium persilicate, urea peroxide and the like. These bleaching agents are only effective at higher temperatures, e.g. from 80°C up to the boil.

It is known that the bleach activity of such percompounds can be improved and becomes effective at lower to medium wash temperatures by the use of organic bleach activators or peroxyacid precursors, of which so far N,N,N',N'-tetraacetyl ethylene diamine (TAED) is the most widely used in practice. These peroxyacid bleach precursors are believed to function by a perhydrolysis reaction with the percompound forming organic peroxyacids which, unlike the percompound, are effective at lower temperatures, e.g. from 30 to 60°C. In the case of TAED, peracetic acid is the peroxyacid liberated in the wash solution.

Various bleach activators or peroxyacid bleach precursors are known in the art, of which a representative but by no means comprehensive list is given below:

- (1) Acyl organoamides of the formula RCONR₁R₂, where RCO is a carboxylic acyl radical, R₁ is an acyl radical, and R₂ is an organic radical, as disclosed in U.S. Patent Specification N ° 3,117,148. Examples of peroxyacid precursor compounds falling under this group are:
 - (a) N,N-diacetylaniline and N-acetylphthalimide;
 - (b) N-acylhydantoins, such as N,N'-diacetyl-5,5-dimethylhydantoin;
- (c) Polyacylated alkylene diamines, such as N,N,N',N'-tetraacetyl ethylene diamine (TAED) and N,N,N',N'-tetraacetyl methylene diamine (TAMD) as disclosed in British Patent N° 907,356;
- (d) Acylated glycolurils, such as tetraacetyl glycoluril (TAGU) as disclosed in British Patent No 1,246,338:
- (e) alpha-Acyloxy-(N,N')-polyacyl malonamides, such as alpha-acetoxy-(N,N')diacetyl malonamide as disclosed in U.S. Patent N° 3,183,266.
- (2) Carboxylic esters of the type as disclosed in British Patent N° 836,988. Examples of activators of this type include phenyl acetate, sodium acetoxy benzene sulphonate, trichloroethylacetate, sorbitol hexaacetate, fructose-pentaacetate, p-nitrobenzaldehyde diacetate, isopropenyl acetate, acetyl aceto hydroxamic acid, and acetyl salicylic acid. Other examples are esters of a phenol or substituted phenol with an alpha-chlorinated lower aliphatic carboxylic acid, such as chloroacetylphenol and chloroacetylsalicylic acid, as disclosed in U.S. Patent N° 3,130,165.
- (3) Acyl-cyanurates, such as triacetyl-or tribenzoylcyanurates, as disclosed in U.S. Patent No 3,332,882.
- (4) Carbonic acid or pyrocarbonic acid esters of the formula R₁OCOOR₂ or R₃OCO-OCO-OR₂, as disclosed in British Patent N° 970,950, for example p-carboxy-phenyl-ethyl-carbonic acid ester, p-carboxyphenyl-ethyl-pyrocarbonic acid ester, and sodium sulpho phenylethyl carbonic acid ester.
- (5) Optionally substituted anhydrides of benzoic or phthalic acid, for example benzoic anhydride, m-chlorobenzoic anhydride and phthalic anhydride.
- (6) Other and similar peroxyacid precursors are disclosed in EP-A-00 98 021; EP-A-01 06 584; EP-A-01 -06-634; EP-A-01 18 304; EP-A-01 20 591; EP-A-01 50 532; EP-A-01 63 331; EP-A-01 74 132 and U.S. Patent Nº 4,283,301.

All these peroxyacid bleach precursors can, in general, be classified as organic compounds having the following general formula:

$$\begin{bmatrix} R(0)_n C - \end{bmatrix}_m L,$$

wherein R is an alkyl, phenyl, aryl or alicyclic radical or a substituted alkyl, phenyl, aryl or alicyclic radical, n is 0-1, m is 1-4, and L is any suitable leaving group which exerts an electron-attracting effect. A leaving group is any group that is displaced from the peroxyacid bleach precursor as a consequence of the nucleophilic attack on the precursor by the perhydroxide anion (OOH⁻). This, the perhydrolysis reaction,

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results in the formation of the peroxyacid. It should be appreciated that the leaving group L may also contain one, two or more reactive or non-reactive carboxylic acyl radicals.

It has now been found that a low to medium temperature bleaching composition having improved bleaching and cleaning effect on multistained fabrics can be obtained if a bleach system is used comprising a percompound and a mixture of at least two peroxyacid bleach precursors

(a)
$$\mathbb{R}_1(0)_n \mathbb{C} \stackrel{\bigcirc}{-} \mathbb{L}$$
 and (b) $\mathbb{R}_2(0)_n \mathbb{C} \stackrel{\bigcirc}{-} \mathbb{L}$,

wherein R_1 is a lower alkyl group containing 1-4, preferably 1-2 carbon atoms, or a phenyl group; R_2 is a higher alkyl, aryl or alicyclic radical (substituted or unsubstituted) containing 6-20, preferably 8-16 carbon atoms; and L, n and m are as defined above.

The peroxyacid precursor mixture usable in the present invention can be composed of any type of the above-mentioned compounds and may be used in the composition in a weight ratio to the percompound of from about 1:1 to 1:100, preferably from 1:1 to 1:50, whereby, for optimal performance and economical reasons, the percompounds should be at least in one mole equivalent to the reactive carboxylic acyl radical of the precursor.

In terms of hydrogen peroxide released by the percompound, a ratio of at least 2 (two) moles of hydrogen peroxide per mole of peroxyacid bleach precursor mixture is preferred, and more preferably higher than 4 (four) moles of hydrogen peroxide per mole of peroxyacid precursor mixture.

Effectively, the hereinbefore described peroxyacid bleach precursors can be used as mixtures in weight ratios within the broad range of from 25:1 to 1:25, preferably from 15:1 to 1:15, more preferably from 5:1 to 1:5.

Preferred examples of peroxyacid bleach precursors of category (a) usable in the mixture of the invention are:

N,N,N',N'-tetraacetyl ethylene diamine (TAED); glucose pentaacetate (GPA); xylose tetraacetate (XTA); sodium or potassium acetoxy benzene sulphonate (SABS); sodium or potassium benzoyloxy benzene sulphonate (SBOBS); tetraacetyl glycoluril (TAGU); alpha-acetoxy(N,N')-diacetyl malonamide; and sodium or potassium p-sulpho phenyl methyl (or ethyl) carbonate.

Preferred examples of peroxyacid bleach precursors of category (b) usable in the mixture of the invention are:

sodium or potassium p-linear octanoyloxy benzene sulphonate; sodium or potassium p-linear nonanoyloxy benzene sulphonate; sodium or potassium p-linear decanoyloxy benzene sulphonate; and sodium or potassium 3,5,5-trimethyl hexanoyloxy benzene sulphonate.

Alternatively, a peroxyacid bleach precursor having said mixture characteristics combined in one molecule

of the formula

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wherein R₁, R₂, L and n are as defined above and m' is 1-3, can also be used.

The invention therefore provides a bleaching or detergent bleach composition comprising a percompound and

i) a mixture of at least two peroxyacid bleach precursors

a)
$$\begin{bmatrix} R_1(0)_n C - \end{bmatrix} - L$$
 and b) $\begin{bmatrix} R_2(0)_n C - \end{bmatrix} - L$,

wherein R₁, R₂, L, m and n are as defined above; or

ii) a peroxyacid bleach precursor of the formula

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$$\begin{bmatrix} R_1(0)_n C - - L - C - (0)_n R_2 \end{bmatrix}_{m}$$

wherein R₁, R₂, L, n and m' are as defined above.

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Normally, the percompound, such as sodium perborate, which may be in the tetrahydrate or monohydrate form, and the peroxyacid bleach precursor mixture can be present in the bleach composition in amounts of from 5-99% by weight and from 50 to 1% by weight, respectively. The bleaching composition of the invention may consist solely of a percompound and the peroxyacid bleach precursor mixture when used as a pure bleach product or as a bleach additive to detergent compositions. In that case the composition will comprise from 50-99% percompound and from 50-1% peroxyacid bleach precursor mixture.

Normally, however, the bleaching composition of the invention will be formulated as a detergent bleach composition and will contain at least one surface-active agent selected from the group consisting of soap, synthetic anionic, nonionic, cationic, amphoteric and zwitterionic detergents and mixtures thereof, in an amount of from about 2 to 40% by weight of the composition.

Generally, mixtures of the above surface-active agents are used; mixtures of synthetic anionic, synthetic nonionic surfactants and soap are commonly used.

Suitable anionic detergent substances are alkali metal soaps of fatty acids, fatty acid-protein condensation products, primary or secondary alkyl sulphates, fatty acid alkanolamide sulphates, sulphated alkyl-or alkylphenol-polyglycolethers, fatty acid isethionates, fatty acid taurides, alkylbenzene sulphonates, alkane sulphonates, olefin sulphonates, salts of alpha-sulpho fatty acids and esters thereof, and other known surface-active compounds of the sulphate and sulphonate type.

Suitable examples of nonionic detergent substances are alkyl and acyl polyglycolethers, alkylphenol polyglycolether, fatty acid alkanolamides and their ethoxylated products, ethoxylated polypropylene glycolethers, amine oxides and fatty acid sugar esters.

Further examples of suitable surface-active compounds commonly used in the art are given in "Surface Active Agents", Volume I, by Schwartz and Perry (Interscience, 1949) and "Surface Active Agents", Volume II, by Schwartz, Perry and Berch (Interscience, 1958).

In addition to the surface-active compounds or mixtures thereof, the bleaching composition of the invention may further and preferably contain detergency builders. Usually the total amount of detergency builders in a detergent composition of the invention will be from about 5% to about 70% by weight of the detergent composition. Many detergency builders are known, and those skilled in the art of formulating fabric-washing detergent compositions will be familiar with these materials.

Examples of known detergency builders are sodium tripolyphosphate; sodium orthophosphate; sodium pyrophosphate; sodium trimetaphosphate; sodium ethane-1-hydroxy-1,1-diphosphonate; sodium carbonate; sodium silicate: sodium citrate; sodium oxydiacetate; sodium nitrilotriacetate; sodium ethylenediaminetetraacetate; sodium salts of long-chain dicarboxylic acids, for instance straight-chain (C10 to (2) succinic acids and malonic acids; sodium salts of alpha-sulphonated long-chain monocarboxylic acids; sodium salts of polycarboxylic acids; i.e. acids derived from the polymerization or copolymerization of unsaturated carboxylic acids and unsaturated carboxy acid anhydrides such as maleic acid, acrylic acid, itaconic acid, methacrylic acid, crotonic acid and aconitic acid, and the anhydrides of these acids, and also from the copolymerization of the above acids and anhydrides with minor amounts of other monomers, such as vinyl chloride, vinyl acetate, methyl methacrylate, methyl acrylate and styrene; polyacetal carboxylates; and modified starches such as starches oxidized, for example, using sodium hypochlorite, in which some anhydroglucose units have been opened to give dicarboxyl units.

Another type of detergency builder which can be used, either alone or in admixture with other builders, is a cation-exchange material, especially a sodium aluminosilicate such as described in GB Patent 1,429,143 or in Netherlands Patent Application 7403381.

Preferred materials of this type have the formula:

(Na₂O) _{0.7-1,1}.Al₂O₃(SiO₂)_{1,3-3,3}

and may be amorphous or crystalline, with some bound water usually in an amount of about 10-30% depending on the drying conditions used. Such water-insoluble aluminosilicate cation-exchange materials are available as very finely divided powder, commercially known under various grades of zeolites, e.g. Zeolite A and Zeolite B.



Furthermore, any other non-interfering ingredients normally used in detergent compositions in minor amounts, which serve to improve the bleaching and laundering characteristics of the composition or which add aesthetic appeal to the composition, may also be incorporated.

One such important minor ingredient serving to improve the bleaching and laundering characteristics is a stabilising agent such as ethylene diamine tetraphosphonic acid or its alkali metal salts as disclosed in GB Patent 1,392,284, and other selected types of compounds as disclosed in GB Patent 2,033,937.

Other minor ingredients can include washing alkalis and buffering agents; sequestering agents such as EDTA; polymeric co-builders; suds-controlling agents; soil-suspending agents and anti-redeposition agents; enzymes, particularly proteolytic enzymes; corrosion inhibitors; optical brighteners, colouring agents, heavy metal catalysts, perfumes, bacteriostats and filler materials.

Generally, such minor components comprise no more than about 20% by weight of the bleach composition.

In such bleach detergent compositions the percompound and peroxyacid bleach precursor mixture will generally be present in amounts of from 5-50% by weight and from 1-25% by weight, respectively, preferably from 6-30% by weight of percompound and 2-15% by weight of precursor mixture.

As explained before, the bleach and/or detergent composition of the invention will have the advantage of being effective in the removal of all sorts of stains from fabrics, which soiling normally occurs in practice under domestic and industrial conditions. Many types of stains have hydrophobic, hydrophilic, proteolytic characteristics either in isolation or combined altogether in one stain. Especially if enzymes are also incorporated, the bleaching detergent composition of the invention will have the advantage of being an improved and effective washing composition for universal use.

It has also the further advantage over detergent bleach compositions based on pure peroxyacid bleach systems that it is more stable and less sensitive to alkalinity.

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The following Examples will now illustrate the invention.

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Examples I-II

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The following granular detergent bleach compositions were prepared by spray-drying a base powder and post-dosing the heat-sensitive ingredients enzyme, perborate and peroxyacid bleach precursors.

	Composition	I	II
		% by weight	% by weight
10	Sodium C ₁₂ linear alkyl benzene sulphonate	8.0	9.0
15	C ₁₂ -C ₁₅ linear alkyl/ 7 ethoxylate	6.0	4.0
	Sodium soap (C ₁₈ fatty acid)	3.0	-
	Sodium tripolyphosphate	30.0	23.0
20	Alkaline sodium silicate (Na ₂ O : SiO ₂ = 1:2.2) Sodium carbonate	6.0 10.0	5.0
25	Ethylene diamine tetraacetate (EDTA)	0.2	0.2
	Ethylene diamine tetraphosphonic acid (EDTMP)	0.3	0.3
, 30	Sodium sulphate	10.0	38.0
	Sodium carboxymethylcellulose (SCMC)	0.5	0.5
35	Fluorescer	0.2	0.2
	Sodium perborate monohydrate	15.0	6.0
	TAED	2.0	2.3
40 .	Sodium 3,5,5-trimethyl hexanoyloxy benzene sulphonat		2.0
	Savinase (R) - proteolytic enzyme		0.5
	Water	7.0	9.0

Washing experiments with these compositions have shown good performance on cleaning multistained fabrics.

Good results were also obtained with the above formulations, but using the following peroxyacid bleach precursor mixtures:

- 1) sodium acetoxy benzene sulphonate and sodium 3,5,5-trimethyl hexanoyl benzene sulphonate.
- 2) sodium acetoxy benzene sulphonate and sodium p-linear nonanoyloxy benzene sulphonate.
- 3) glucose pentaacetate and sodium p-octanoyl benzene sulphonate.
- 4) tetraacetyl glycoluril and sodium 3,5,5-trimethyl hexanoyloxy benzene sulphonate.
- 5) sodium p-benzoyloxy benzene sulphonate, sodium acetoxy benzene sulphonate and sodium 3,5,5-trimethyl hexanoyloxy benzene sulphonate.
 - 6) tetraacetyl ethylene diamine and p-linear nonanoyloxy benzene sulphonate.

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Claims

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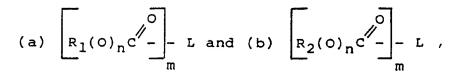
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Bleaching or detergent bleach composition comprising a percompound and
 i) a mixture of at least two peroxyacid bleach precursors



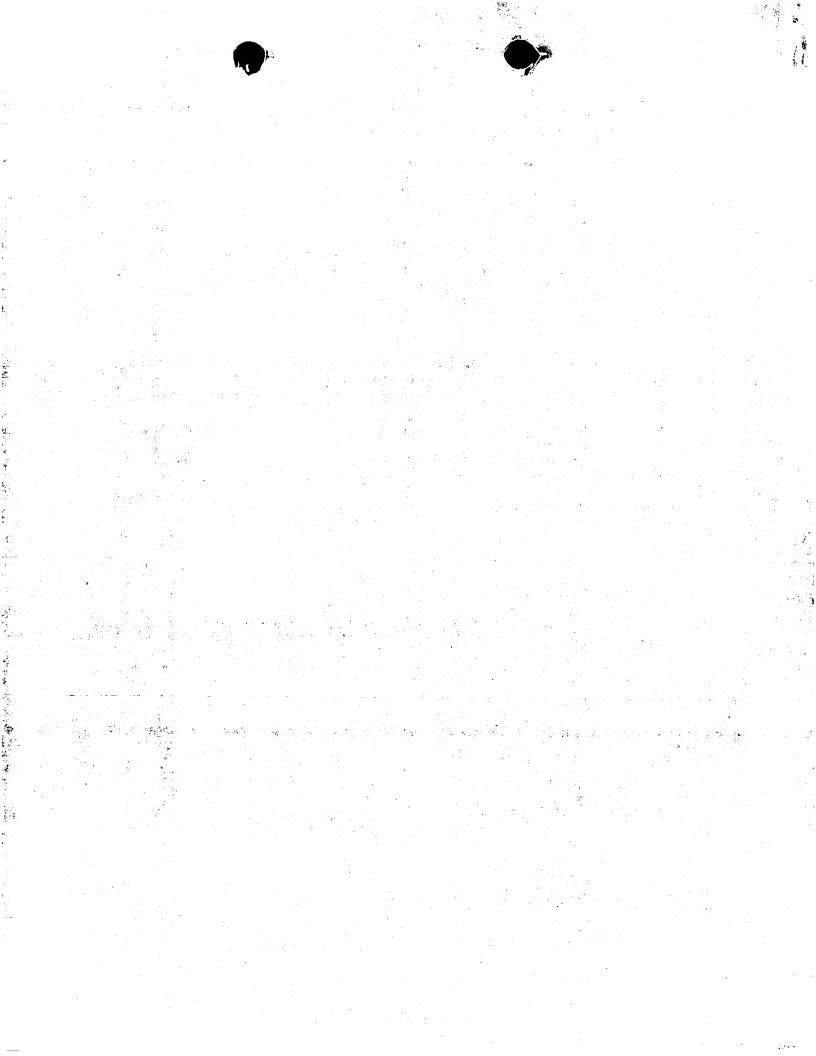
wherein R_1 is a lower alkyl group containing 1-4 carbon atoms, or a phenyl group; R_2 is a higher alkyl, aryl or alicyclic radical (substituted or unsubstituted) containing 6-20 carbon atoms; n is 0-1; m is 1-4 and L is a leaving group which exerts an electron-attracting effect, or

ii) a peroxyacid bleach precursor of the formula

$$[R_1(0)_n C] - [-C] - [0]_n R_2$$

wherein R₁, R₂, L and n are as defined above, and m' is 1-3.

- 2. Bleaching or detergent bleach composition according to claim 1, characterized in that it further contains at least one surface-active agent.
- 3. Bleaching or detergent bleach composition according to claim 1 or 2, characterized in that it further contains a detergency builder in an amount of from 5 to 70% by weight.
- 4. Bleaching or detergent bleach composition according to claim 2 or 3, characterized in that it comprises from 5-50% by weight of percompound and from 1-25% by weight of peroxyacid bleach precursor.











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(5) Improved bleaching or detergent bleach compositions are disclosed which comprise a percompound, such as sodium perborate, and

i) a mixture of at least two peroxyacid bleach precursors

(a)
$$\begin{bmatrix} R_1(0)_n C \end{bmatrix} - L$$
 and (b) $\begin{bmatrix} R_2(0)_n C \end{bmatrix} - L$

wherein R₁ is a lower alkyl group containing 1-4 carbon atoms, or a phenyl group; R2 is a higher alkyl, aryl or alicyclic radical (substituted or unsubstituted) containing 6-20 carbon atoms; n is 0-1; m is 1-4 and L is a leaving group which exerts an electron-attracting effect, or

ii) a peroxyacid bleach precursor of the formula

$$\begin{bmatrix} R_{1}(0)_{n} C & - \\ - \\ - \\ - \end{bmatrix}_{m} L - \begin{bmatrix} C & - \\ - \\ - \end{bmatrix}_{n} C \begin{bmatrix} C & - \\ - \\ - \end{bmatrix}_{m},$$

wherein R₁, R₂, L and n are as defined above, and m' is 1-3. The compositions show improved bleaching and cleaning effect on multistained fabrics.



EUROPEAN SEARCH REPORT

Application Number

EP 87 20 1546

	DOCUMENTS CONSI	DERED TO BE RELEVA	INT	
ategory	Citation of document with in of relevant pa	ndication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 098 129 (PR * Examples 2,3,7,8, - page 10, line 12	13; page 9, line 20	1-4	C 11 D 3/39
х	EP-A-O 120 591 (PR * Examples 16,18,19		1,4	
Х	BE-A- 674 217 (FM * Claims *	C)	1-4	
A	EP-A-O 163 331 (PR * Page 9, lines 9-2		1-4	
				TECHNICAL FIELDS SEARCHED (Int. Cl.4)
				C 11 D D 06 L
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	The present search report has b	een drawn up for all claims		
Place of search		Date of completion of the search		Examiner
THI	E HAGUE	10-02-1988	coud	CKUYT D.E.
CATEGORY OF CITED DOCUMEN X: particularly relevant if taken alone Y: particularly relevant if combined with and document of the same category A: technological background O: non-written disclosure		E: earlier pater after the fil other D: document c L: document c	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding	